

Semifluorinated Aromatic Side-Group Polystyrene-Based Block Copolymers: Bulk Structure and Surface Orientation Studies

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Introduction: The goal of this research was to develop new block copolymers bearing fluorinated substituents containing aromatic groups in the side chains, capable in principle of improving the properties of the surface by exploiting the enhanced self-assembly behavior of the semifluorinated side groups containing a phenyl ring. Bearing this idea in mind we synthesized two series of new fluorinated block copolymers by following two different synthetic paths, on one hand using the polymer-analogous modification reaction of the side chains of preformed anionically polymerized poly(styrene-*b*-isoprene) block copolymers and on the other the controlled radical polymerization of fluorinated styrene monomers.

Methods and Materials: The surface organization was evaluated by near-edge X-ray absorption fine structure (NEXAFS). The effects of the phenyl ring on the orientation of the fluorinated substituent at the surface was elucidated by relating the surface order parameter of the $-\text{CF}_2-$ helix, $S_{\text{C-F}}$, with the surface order parameter of the phenyl ring normal, S_{π^*} . The structure of the fluorinated surface as elucidated by NEXAFS was correlated to the wetting behavior of the materials.

Results: The effects of the phenyl ring and the fluorocarbon pendent groups on the surface and bulk structure of materials were investigated. NEXAFS measurements showed high $-\text{CF}_2-$ helix surface orientation parameters which remained relatively unchanged after prolonged exposure of the polymer films to water. The surface orientational order parameters of the aromatic fluorinated side-chain block copolymers also proved to be consistently higher than the previously investigated semifluoroalkyl side-chain block copolymers. NEXAFS also allowed us to determine the surface orientational order parameter S_{π^*} of the phenyl group normal. In both types of polymers, the CF_2 helix surface orientational order parameter turned out to be strongly coupled to the phenyl ring order parameter when the number n of CF_2 groups was equal to 8 (Figure 1). In particular, in the anionically polymerized block copolymers S_{π^*} turned out to be slightly smaller than the $S_{\text{C-F}}$, whereas in the CRP block copolymers S_{π^*} was slightly larger than $S_{\text{C-F}}$. This difference can be explained on the basis of the different chemical structures. In particular, the flexible spacer between the phenyl ring and the polymer main chain in the former system could give the phenyl ring more flexibility, thus resulting in a smaller S_{π^*} value. On the other hand, the phenyl ring directly linked to the polymer backbone in the latter system, would result in a less flexible side chain thus leading to a larger S_{π^*} value.

Conclusions: The introduction of an aromatic ring between the polymer backbone and the fluorocarbon pendent group turned out to improve the self-assembly behavior of the fluorinated part of the side chain at the surface. This self-assembly produces highly hydrophobic $-\text{CF}_3$ surfaces that are remarkably stable towards reconstruction upon exposure to water.

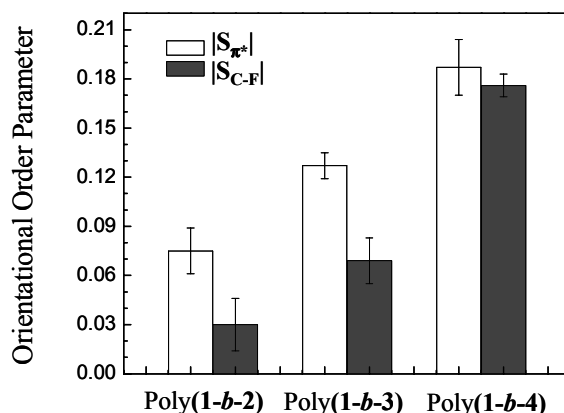


Figure 1 Direct comparison of orientational order parameters (S_{π^*} and $S_{\text{C-F}}$) for block copolymers Poly(1-b-2) (n=4), Poly(1-b-3) (n=6) and Poly(1-b-4) (n=8) produced by controlled radical polymerization. The y-coordinate is plotted as the absolute value of the (negative) orientational order parameters. When the number n of $-\text{CF}_2-$ units is equal to 8, S_{π^*} is almost equal to $S_{\text{C-F}}$ and the phenyl ring is collinear with the CF_2 helix.